PB-221 177

WORKSHOP ON MATHEMATICAL MODELING OF PHOTOCHEMICAL SMOG: SUMMARY OF THE PROCEEDINGS. OCTOBER 30-31, 1972

Marcia C. Dodge

National Environmental Research Center

Prepared for:

Environmental Protection Agency

January 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 221 177

EPA-R4-73-010
January 1973

Environmental Monitoring

Workshop on Mathematical Modeling of Photochemical Smog: Summary of the Proceedings

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA 22151

Office of Research and Monitoring
National Environmental Research Center
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-R4-73-010	2.	3. Recipient's Accession No. PB-221 177
4. Title and Subtitle: Workshop on Mathematical Modeling of Photochemical Smog: Summary of the Proceedings October 30-31, 1972			5. Report Date: January 1973 6.
7. Author(s): Marcia C. Dodge			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: ENVIRONMENTAL PROTECTION AGENCY, National Environmental Research Center, Chemistry and Physics Laboratory, Research Triangle Park, North Carolina 27711			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address: Same			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstracts

A workshop on modeling of photochemical smog was held for two main reasons. One purpose was to establish lines of communication between the person gathering the data and the person who is using the data to formulate a photochemical model. The second purpose was to determine those key areas where further research is needed. The papers and discussions presented during the workshop may be classified under the following subject areas: The Role of Kinetic Studies in Modeling; The Role of Smog Chamber Experiments in Modeling; The Role of Atmospheric Measurements in Modeling.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Mathematical models
Photochemical reactions
Smog
Reaction kinetics
Test chambers
Aerosols

17b. Identifiers/Open-Ended Terms

Airsheds

17c. COSATI Field/Group 13B

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Unlimited	UNCLASSIFIED	56
	20. Security Class (This Page) UNCLASSIFIED	22. Price 3.00

FORM NTIS-35 (REV. 3-72) USCOMM-DC 14952-P72

EPA-R4-73-010

Workshop on Mathematical Modeling of Photochemical Smog: Summary of the Proceedings

October 30-31, 1972

by

Marcia C. Dodge

Chemistry and Physics Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

National Environmental Research Center
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

January 1973

TABLE OF CONTENTS

		Page
I.	STATE OF THE ART	
	A. Introduction	1
	B. State of the Art of Photochemical Modeling Philip M. Roth	4
	C. State of the Art of Atmospheric Chemistry Thomas A. Hecht	10
II.	THE ROLE OF KINETIC STUDIES IN MODELING	
	A. Photolysis of NO_2	12
	B. Reaction of O_3 and NO_2	12
	C. Reaction of N_2O_5 and H_2O	13
	D. Reaction of OH and CO	14
	E. Reaction of HO_2 and NO	15
	F. Reaction of Olefins and O Atoms	15
	G. Reaction of Olefins and O_3	16
	H. Reaction of Olefins and OH	17
	I. Reaction of Olefins and HO_2, RO, and RO_2	17
	J. Reactions of Alkoxy Radicals	17
	K. Photolysis of Aldehydes	18
III.	THE ROLE OF SMOG CHAMBER EXPERIMENTS IN MODELING	
	A. The Modeling of Smog Chamber Data	
	1. Alan Eschenroeder	19
	2. Thomas A. Hecht	21
	3. Lowell G. Wayne	23
	Discussion	25

Page

B. Proposed Smog Chamber Study to Aid in the Modeling Effort - Harvey Jeffries 26

C. The Role of Aerosols in Photochemical Smog Arthur Levy 28

IV. THE ROLE OF ATMOSPHERIC MEASUREMENTS IN MODELING

A. Recommendations for Future Field Studies Alan Eschenroeder 30

Discussion. 32

B. Los Angeles Reactive Pollutant Study William A. Perkins. 34

C. Coupling of the Photochemistry to an Airshed Model Ralph C. Sklarew. 35

Discussion. 37

D. Summary 39

APPENDIX A.

The Chemistry of Photochemical Smog Formation A-1

APPENDIX B.

Workshop Participants B-1

I. STATE OF THE ART

A. Introduction

This workshop on the modeling of photochemical smog formation was held for two principle reasons. One purpose was to establish lines of communication between the experimentalist and the modeler.... between the person gathering the data and the person who is using the data to formulate a photochemical model. In the past there had been too little interaction between the groups. It was important to define the problems facing both the experimentalist and the modeler, to recognize the limitations of each endeavor and to determine what could and what could not be accomplished.

Realizing that more research must be undertaken before the full potential of modeling can be realized, the second purpose of this meeting was to determine those key areas where further research is needed.... to determine how best to attack the problem of providing the necessary data to enable development of a model capable of predicting air quality.

The Chemistry and Physics Laboratory has an extensive program underway to elucidate the chemistry of photochemical smog formation. The Laboratory carries out research in two principle areas; it develops information on the chemical and physical transformations that pollutants undergo in the atmosphere and it develops techniques and instruments for the measurement of these pollutants. Some of the activities that the Laboratory is engaged in to furnish information on atmospheric chemistry are the following:

1. Smog chamber studies to....

(a) Investigate the relationship between hydrocarbons and the rate of conversion of NO to NO_2.

(b) Determine the role of aerosols.

(c) Identify SO_2 removal and oxidation processes.

2. Field studies to determine....

(a) Background levels of hydrocarbons.

(b) Transport of O_3 beyond an urban area.

(c) Fate of reactive pollutants.

3. A 5-year Regional Air Pollution Study of St. Louis during which the Chemistry and Physics Laboratory will be performing such tasks as....

(a) Field testing new analytical instruments.

(b) Measuring trace gases, such as acetylene and CO, to determine the contribution of auto exhaust to urban pollution.

(c) Performing detailed compositional analyses of hydrocarbons.

(d) Determining the mass and size distribution, concentration and chemical composition of aerosols.

4. The development of new instrumentation to aid in the detection of atmospheric pollutants. Some of the instruments under development are....

(a) Fourier Transform Infrared Spectrometer coupled to a long path cell for the analysis of trace constituents at the ppb level.

(b) High energy light sources such as tunable diode lasers for <u>in situ</u> measurements of gaseous pollutants.

(c) New optical techniques such as remote lidar systems for measuring stack effluents and particulates.

(d) New instruments to aid in the characterization of aerosols.

In addition to the above areas of research, the Chemistry and Physics Laboratory has recently initiated a program to develop the optimum photochemical mechanism that can be satisfactorily coupled with emission and meteorological models to assess air quality. In addition to plans currently underway to carry out new smog chamber studies and to measure rates of reaction, a contract has been awarded to develop such a photochemical mechanism and to test this mechanism against chamber data. Because of this commitment to modeling and a desire to concentrate efforts in a manner that will yield the most critically needed information, this workshop was organized with the hope that the resulting discussions would aid in developing future directions for the modeling effort.

B. State of the Art of Photochemical Modeling - Philip M. Roth

Systems Applications, Inc., with P. Roth as project officer, is currently under contract to the Chemistry and Physics Laboratory to develop a photochemical mechanism and to test this mechanism using smog chamber data.

P. Roth began his presentation on the state of the art of photochemical modeling with a description of the use of models as predictive tools. One use of models is to simulate the effects of alternative air pollution control strategies on pollutant concentrations. Another use of models is for land use planning so that projected freeways and power plants may be located where their air pollution potential is minimized. Models can be used for planning long-term control strategy to accomplish air quality objectives at least cost. Another use of models is to enable real-time prediction in an alert warning system to anticipate impending air quality episodes.

Several types of models have been formulated in an effort to meet these modeling needs. The simplest of these is the box model, where pollutant concentrations are assumed to be homogeneous throughout the entire airshed. A second type of model, developed to describe the concentration of inert species downwind of a point source, is the gaussian plume model. Both of these models are too simple to meet the requirements of modeling. A more complex approach is one based on the solution of the equations of continuity. This approach provides the means for including chemical reactions,

time-varying meteorological conditions, and complex source emission patterns. Finally, the most complex model proposed involves the solution of the full boundary layer equations for the conservation of mass, momentum and energy. Since the solution of these equations exceeds the capabilities of present generation computers, the thrust of the current program is on developing models based on the solution of the continuity equations.

Two main types of airshed models, based on the solution of these continuity equations, are currently under development. One is the trajectory or moving coordinate approach where a hypothetical column of air is followed through the airshed as it is advected by the wind. This model is useful for describing the concentration of species downwind of a point source, line source or area source. The other is the grid or fixed coordinate approach where the airshed is divided into three-dimensional cells, each cell perhaps one or two miles on a side and about 100 feet high. This model is useful for describing pollutant concentrations throughout the airshed. These two approaches are based on the finite difference solution of the equations of conservation of mass. These equations are composed of....

1. terms to describe how pollutants are transported by winds and dispersed by turbulent air motions

2. source terms to describe the influx of new pollutants

3. sink terms to account for the removal of materials

...and 4. chemical reaction terms.

For every chemical species in the mechanism, a differential equation must be written. Since these equations are coupled through the reaction rate terms, they must be solved simultaneously. Therefore, the time for solution increases with each new species added to the mechanism. For this reason, it is crucial to use as few species as possible in formulating a mechanism. At the same time, however, a sufficient number must be included in order to maintain some semblance of reality. In essence, it is necessary to achieve a proper balance between chemical accuracy in prediction and computational simplicity, remembering that the kinetic model is only one part of the overall airshed model.

There are many uncertainties associated with the various input variables to this conservation of mass equations. Emission strengths are imprecisely known. For example, auto emissions are estimated from a laboratory driving cycle which may or may not be representative of actual driving patterns. Meteorological considerations introduce a large uncertainty. Information on such variables as inversion heights, boundary conditions and wind speeds aloft is scanty. There is considerable uncertainty in the air quality data. The accuracy of the data, the frequency of the measurements, and the number and distribution of the sampling stations in general is inadequate.

Another area of uncertainty -- and the area this workshop addressed itself to -- is the chemistry of atmospheric transformation processes. A number of unresolved problems are associated with

this complex subject. The role of aerosols in smog formation has not been elucidated satisfactorily. The effects of the size, mass, and chemical composition of aerosols on atmospheric processes are not well defined. Likewise, the role of SO_2 in photochemical smog formation is not well characterized. For these reasons, neither SO_2 nor aerosol chemistry has as yet been modeled. Little is known about sinks for pollutants. The importance of soil as a sink for CO and of vegetation as a sink for SO_2 and NO_2 has not been determined. The rates of a number of chemical reactions and the elementary steps and reaction products of certain other reactions are unknown. Some species suspected of playing a role in smog formation, such as HNO_3, have not been detected in the atmosphere. The effects of temperature, especially on the heterogeneous reactions, have not been determined. Plume chemistry is little understood. The effect of high temperature and high concentrations on the chemistry of stack effluents is not well defined. These problems demonstrate how difficult it is in some cases to relate the chemistry occurring in smog chambers to that which is occurring in the atmosphere.

The successful development of a comprehensive airshed model depends heavily on the accurate description of reaction rate processes. Only in the last several years have investigators postulated general kinetic mechanisms to describe the rates of chemical reactions in the atmosphere. Three classes of mechanisms

have been postulated to explain atmospheric chemistry. There were the early mechanisms of Friedlander and Seinfeld, Eschenroeder, and Behar that were highly simplified, consisting of fewer than ten reactions. Later in the development came less simplified mechanisms consisting of 10-25 steps. The Hecht and Seinfeld and the Eschenroeder and Martinez mechanisms fall in this category. Also developed at this time were the highly complex mechanisms such as Wayne's 33 step mechanism, Niki's 60 step propylene mechanism, Calvert's multistep mechanisms, Levy's tropospheric model and Johnston's stratospheric model. Only the mechanisms of Hecht and Seinfeld, Eschenroeder and Martinez, and Wayne have been incorporated into urban airshed models.

Since for each species added to the mechanisms, a new equation must be written and solved simultaneously with the other equations, lumping is desirable. There are various ways to lump. Fast and slow reactions can be combined, thus eliminating the fast reacting intermediates. Hydrocarbons may be lumped, either as a single "species" or perhaps one "species" for olefins, one for aromatics, and one for paraffins. Radicals may be lumped into general classes such as alkyl, alkoxy and peroxy. Steady-state assumptions can be made to eliminate differential equations for transient species such as O atoms and OH radicals. One of the more difficult problems facing the modeler is determining just what lumps should be used. It is a formidable task both to select

the groupings and to decide what parameters for these groupings should be employed in the rate expressions.

Once a mechanism has been formulated, it is necessary to test this mechanism against laboratory data. The determination of just what experimental programs should be undertaken to facilitate the validation of these photochemical models was a prime objective of this workshop.

C. State of the Art of Atmospheric Chemistry - Thomas A. Hecht

T. Hecht is a graduate student at the California Institute of Technology who, in conjunction with Professor John Seinfeld, has developed a generalized mechanism for photochemical smog formation. He is currently a consultant to Systems Applications, Inc., assisting P. Roth in carrying out further refinements of the chemical model.

T. Hecht distributed a list of some 40 reactions that are either known or suspected to be of importance in explaining the chemical processes occurring in polluted atmospheres [see Appendix A]. He discussed these reactions, emphasizing the uncertainties that are associated with each. He pointed out those reactions for which the rate constants are either unknown or the rate constants are imprecisely determined, and therefore highly suspect. Those reactions for which the intermediates and products of reaction are unknown were also discussed and possible mechanisms for each were offered.

In addition to discussing each reaction in detail, Hecht raised several questions on the possible effect of particulate matter and surface area atmospheric reactions. Do particles accelerate the oxidation of NO? Do they terminate radical chains? How does the water content of particles and size, number and chemical composition of aerosols influence atmospheric reaction?

The problems of relating smog chamber chemistry to atmospheric processes were mentioned. The possible effects of surface-to-volume ratio, stirring of the chamber, nature of the

walls, and the relationship between the chamber hydrocarbon compositions and their concentrations to those of the atmosphere were discussed. Questions were raised on the possible effect of H_2O, temperature and light intensity on the rates of reaction.

II. THE ROLE OF KINETIC STUDIES IN MODELING

An open discussion was held of each of the reactions listed in T. Hecht's handout [see Appendix A]. The following is a brief description of some of the more important reactions considered and the comments that were raised.

A. Photolysis of NO_2

The point was raised that the results of validation studies indicate that $k_a\emptyset$ for the reaction $NO_2 + h\nu \rightarrow NO + O$ is one of the most important parameters in a smog chamber experiment. Small changes in $k_a\emptyset$ in the simulations produce large changes in the time to the NO_2 maximum and the amount of O_3 formation. The rate of photolysis in both smog chamber experiments and in the atmosphere is uncertain by about 20%. W. Perkins discussed his plans for developing a new actinometer for use in the field that will measure the rate of dissociation of NO_2 in an atmosphere of nitrogen. T. Hecht mentioned the difficulty of relating k_d to $k_a\emptyset$ and told how he and J. Seinfeld have worked out a means of calculating $k_a\emptyset$ without first measuring k_d. J. Pitts indicated that a possible solution to these problems might be to use O-nitrobenzaldehyde as an actinometer.

All participants agreed that a more accurate means of measuring the rate of photolysis of NO_2 is necessary.

B. Reaction of O_3 and NO_2

It was pointed out that two determinations of the rate

of the reaction $O_3 + NO_2 \rightarrow NO_3 + O_2$ have been made. Johnston and Yost obtained $k = 0.11$ ppm^{-1} min^{-1} and Ford et al measured $k = 0.048$ ppm^{-1} min^{-1}. The point was raised that some modelers are finding that the build-up of O_3 is underestimated when even the smaller of these measured values is used in their simulations. H. Johnston pointed out that he is re-investigating this reaction and that preliminary results indicate that his earlier value may be too high. However, H. Niki who also is re-investigating this reaction indicated that his results support Johnston's earlier value. Johnston suggested that perhaps the photolysis of NO_3 should be taken into account to reduce the NO_3 levels in the simulations and thereby increase the predicted levels of ozone to bring them more in line with the experimental results.

C. Reaction of N_2O_5 and H_2O

The only measured value of the reaction $N_2O_5 + H_2O \rightarrow 2HNO_3$ is Jaffe and Ford's value of 2.5×10^{-3} ppm^{-1} min^{-1}. H. Johnston pointed out that this reaction does not take place in the gas phase but occurs only on surfaces. It is agreed that this reaction does take place in both the atmosphere and in the smog chamber. The difficulty comes in trying to asses the relative importance of this reaction in the two environments. H. Niki felt that heterogeneous reactions occur to a greater extent in the smog chamber than in the atmosphere. The surface-to-volume ratio in a smog chamber is greater than in the atmosphere even

though the atmospheric particulate loading is high. A. Eschenroeder supported this view. A.P. Altshuller raised the issue that it is not only the particulate matter in the atmosphere that must be considered, but also, one must take into account the many rough surfaces at ground level which offer ready sites for heterogeneous reactions.

H. Levy pointed out that, on the basis of some calculations he has made, he estimates the atmospheric concentration of HNO_3 to be 50 ppb. P. Hanst spoke of the Laboratory's long path infrared system and the attempt to see HNO_3 in the gas phase. Largely because of instrumental problems, this endeavor has been unsuccessful to date. It was agreed by most in attendance that every effort to measure HNO_3 in the atmosphere and every means to determine the effect of various surfaces on the rate of this reaction should be made.

D. Reaction of OH and CO

The rate constant for the reaction $OH + CO \rightarrow CO_2 + H$ is fairly well established to be 240 ± 30 ppm^{-1} min^{-1}. The point in some dispute is whether or not this reaction is of any importance in the atmosphere. Several investigators have found that this reaction does not compete with the much faster olefins and OH reactions. J. Bufalini pointed out that experiments conducted in the large irradiation chamber at realistic concentrations showed that, even when only paraffins were present, 20 ppm CO had to be

added to the system before an effect could be observed. W. Wilson pointed out that, while this reaction is probably unimportant in urban areas, it could play a late-time role in rural areas where the reactive pollutants have been depleted and CO could compete with the slower reacting hydrocarbons for OH radicals. It was pointed out that since the concentration of CO can be lumped into the rate constant, this reaction adds no new species to a generalized smog mechanism and its inclusion in the reaction scheme will not significantly increase computational time. Therefore, this reaction probably should be left in the mechanisms.

E. Reaction of HO_2 and NO

The rate of the reaction $HO_2 + NO \rightarrow OH + NO_2$ is largely unknown. There are several estimates of this rate constant in the range of about 500 ppm^{-1} min^{-1}. If this reaction is the only one of any importance in the atmosphere for the removal of HO_2, then it is not necessary to know precisely the rate of this reaction. The only other suggested removal path for HO_2 is the reaction of HO_2 with olefins. D. Hendry mentioned that he is currently looking into the rates of HO_2 and olefin reactions in the liquid phase and his preliminary results indicate that these reactions are extremely slow, of the order of only 10^{-4} ppm^{-1} min^{-1}.

F. Reaction of Olefins and O Atoms

Rate constants have been measured for most hydrocarbon - O atom reactions of atmospheric interest. The uncertainties lie,

not with the rate constants, but rather with the products of the reaction of olefins with O atoms in the presence of O_2. Modelers are presently limited by a lack of information on the free radical intermediates of olefin - O atom reactions. The results of the simulations are quite dependent on the chain lengths of free radicals that are assumed in the model. It was brought up that chain initiation by olefin - O atom reactions may be more important in smog chambers than in the atmosphere. H. Johnston pointed out that in the atmosphere there is a ready source of OH radicals from the photolysis of HONO which can initiate smog formation. Since reactions of OH radicals with hydrocarbons are several orders of magnitude faster than reactions with O atoms, initiation by O atoms in the atmosphere may be of minor importance. However, it was agreed that, if possible, the mechanism of olefin and O atom reactions in the presence of O_2 should be investigated. As D. Hendry pointed out, this is no easy task since, as soon as O_2 is introduced, O_3 is formed and one is faced with the task of sorting out the olefin - O_3 reactions.

G. Reaction of Olefins and O_3

It is known that O_3 adds to olefins to form a zwitterion or a biradical type intermediate, but the subsequent reactions of this intermediate are unknown. Most in attendance felt that olefin - O_3 reactions are probably of less importance in the atmosphere than in the smog chamber. However, it would help model development to elucidate the mechanism and the products of reaction

H. Reaction of Olefins and OH

All participants agreed that the most important free radical responsible for hydrocarbon consumption is the hydroxyl radical. While a number of rate constants for olefins - OH reactions have been measured, the mechanism and the products of these reactions under atmospheric conditions are unknown. Due to the extreme importance of these reactions in smog formation, major emphasis should be placed on elucidating the mechanisms of these reactions.

I. Reaction of Olefins and HO_2, RO and RO_2

Of those in attendance no one felt that the reactions of hydrocarbons with species other than O, O_3 and OH are of significant importance in explaining smog formation.

J. Reactions of Alkoxy Radicals

Three major reactions are postulated to account for the disappearance of RO reactions:

$$RO + O_2 \rightarrow HO_2 + \text{aldehyde}$$

$$RO + NO \rightarrow RONO$$

$$RO + NO_2 \rightarrow RONO_2$$

The rate constants for these reactions are unknown. It was agreed that it is important to determine the relative ratio of these reactions since the reaction of RO with O_2 is chain propogating whereas reactions with NO and NO_2 are chain terminating.

K. Photolysis of Aldehydes

Of those in attendance, most felt that aldehydes play an important role in smog formation. K. Demerjian commented that a major part of the initial push to oxidize NO and olefins in the atmosphere could come from the photolysis of aldehydes since one of the primary processes yields HCO radicals which in turn are oxidized to HO_2. J. Bufalini commented that studies carried out in his laboratories showed that the presence of aldehydes had a pronounced effect on the rate of reaction. He stated that when acetaldehyde was added to a mixed hydrocarbon - NO_x system a rapid acceleration in the rate of oxidation of NO to NO_2 occurred. However, when benzaldehyde was added to this system, a marked decrease in the rate of oxidation of NO was observed and a significant decrease in O_3 formation occurred. It was agreed that the role of aldehydes in smog formation deserves careful attention. K. Demerjian and J. Pitts stated that the quantum yields of the primary photolysis of aldehydes as a function of wavelength are not well determined and should be further studied.

III. THE ROLE OF SMOG CHAMBER EXPERIMENTS IN MODELING

A. The Modeling of Smog Chamber Data

For the past several years three groups have been under contract with EPA to develop photochemical models. As part of this effort these concerns have been testing their mechanisms with smog chamber data furnished to them by the Chemistry and Physics Laboratory. The following reports are recommendations that three of the individuals involved in this modeling effort had to offer regarding the type of smog chamber data they feel is needed to aid in the modeling effort.

1. Alan Eschenroeder - General Research Corporation

A. Eschenroeder had several suggestions on the type of smog chamber data he feels would help in the validation of models. Some of the suggestions he offered were:

(a) Analysis of reactants and products should be made in situ if possible in order to yield real-time concentrations.

(b) In addition to gas-phase smog chamber experiments, controlled investigations of the effects of aerosol should be carried out. Aerosols should be introduced in a controlled fashion into the chamber to determine the magnitude of heterogeneous reactions.

(c) If possible, nitrogen balances should be achieved in the chamber experiments in order that the wall effects may be ascertained. At the moment, considerable difficulty is being encountered by some of the modelers in attempting to sort out the role of aerosol and wall reactions from gas phase reactions.

(d) If possible, it would be of benefit to the modeler in determining how valid his mechanism is to measure the concentrations of the free radicals, especially hydroxyl and alkyperoxyl radicals, to within an order of magnitude.

(e) It would be desirable to carry out smog chamber experiments under conditions that would result in ozone levels of the concentrations set in the air quality criteria documents. The modelers are currently analyzing atmospheric data that has O_3 levels of 30 pphm. Their results cannot be extrapolated down to the air quality levels of 8 pphm with any confidence. For small increments of control it is believed that the model can be applied with confidence. However, for drastic changes in pollutant levels, the uncertainty of the predictions is high.

(f) More information to aid in model development can be gained through the study of the simpler systems, such as binary hydrocarbon - NO_x systems, than by attempting to fit the complex systems such as smog chamber studies of dilute auto exhaust.

(g) Measurements of all major reactants and products need not be measured to greater than 20% accuracy. It is important that smog chamber experiments be designed that will afford this accuracy of measurement.

2. Thomas A. Hecht - Systems Applications, Inc.

The following are suggestions put forth by T. Hecht as to the type of chamber data he feels is necessary to aid in model validation.

(a) The relative humidity of the smog chamber runs should be controlled and carefully measured.

(b) Temperature rise in the smog chamber should be kept to a minimum. In order that the effect of increasing temperature can be taken into account, the temperature should be measured throughout the run.

(c) The light intensity of the chamber should be determined with the highest possible accuracy. It is important that the light intensity either remain constant throughout the run or that it at least be well defined.

(d) Since the time required to reach the NO_2 peak and the amount of O_3 produced depends greatly on $(NO_2)_o$, it is most important that the initial concentration of NO_2 in the smog chamber runs be accurately determined.

(e) The experimental errors associated with each measurement should be determined and reported. It is difficult to assess the validity of a fit when the experimental uncertainties are unknown.

(f) It would be of value to monitor nitric and nitrous acid concentrations in future studies, if it is possible. Determination of wall concentrations of these species would also be desirable.

(g) In order to assess chamber effects and to determine the reproducibility of the experimental technique, single hydrocarbon component systems should be studied. In order to fine tune existing mechanisms and to determine synergistic effects, it would be valuable to have accurate data for binary mixtures of high and low reactivity hydrocarbons.

(h) Experiments to elucidate the role of aerosols, the effects of mixing, and the effects of dilution would be of benefit.

3. Lowell G. Wayne - Pacific Environmental Services

L. Wayne stated that it is impossible to specify the type of data needed for model validation unless one has a clear idea of the purpose to be served by the model. He raised the question of whether modeling is being done for its own sake -- to prove that it can be done -- or for the sake of establishing control strategy and emergency warning systems. What are the objectives of modeling? Are we building a functional model or an aesthetic one?

When aesthetic considerations dominate, the chemist tends to become overly concerned with the accuracy of rate constants while the non-chemist becomes overly concerned with turbulence effects. As a chemist, Wayne desires to know as much as possible about the elementary reactions and their rate constants in order to have a complete and accurate mechanism. As a modeler, however, he finds himself faced with the necessity of resorting to lumped parameters, and the problem of determining how much lumping can be done before a mechanism becomes too generalized to serve its purpose.

If the model is to meet functional criteria, it should be detailed enough to permit extrapolation with reasonable confidence to ambient air quality concentration levels. To achieve this, appreciable amounts of experimental data must become available for these low concentration ranges or the mechanism

must be detailed enough that varying concentrations will not affect it. Both avenues should be explored.

For control strategy evaluation, it is more important to have adequate chemistry built into a model than to have a detailed accounting of the wind fluctuations. Wayne advocates that the chemical mechanism be tested independently of the meteorology through the analysis of smog chamber data. The validation of atmospheric simulation models by testing against atmospheric data is a necessary step for generating confidence in the model, but it is not an adequate procedure for authenticating the chemical mechanism contained in the model.

Discussion

J. Pitts commented on the new smog chamber research facility under construction at the Statewide Air Pollution Research Center and the efforts underway to establish a program to furnish critically needed information. He urged the modelers to furnish the smog chamber community with a list of priorities to aid them in designing experiments. He especially wanted to know how much emphasis should be placed on getting detailed product analysis.

Most of the participants felt that more complete product analyses should be carried out in future studies. K. Demerjian stated that measurements of methyl nitrate, HNO_3 and H_2O_2, in particular, would aid him in his modeling efforts.

A.P. Altshuller raised the point that collecting atmospheric data is far more costly than performing smog chamber irradiations. Therefore, any information that can be extrapolated from controlled experiments should be obtained in this medium rather than carrying out expensive atmospheric studies. He also questioned the modelers as to how detailed a hydrocarbon analysis of complex smog chamber mixtures is necessary. Due to the expense and the experimental difficulties encountered in such analyses, there is no point in carrying out exhaustive hydrocarbon analyses if the modelers can't use them.

B. Proposed Smog Chamber Study to Aid in the Modeling Effort - Harvey Jeffries

H. Jeffries discussed a novel type of chamber study soon to be initiated by L. Ripperton's group at the University of North Carolina under EPA sponsorshop. This chamber facility is being constructed out-of-doors in a rural community near Research Triangle Park. The structure will consist of an A-frame, covered with transparent Teflon film, that will be divided into two halves, each with a volume of 6,000 cubic feet. Each half of the chamber will be filled with the relatively clean rural air and then the chambers will be charged with varying amounts of hydrocarbons and NO_x. Irradiations will be carried out under conditions of natural sunlight, temperature, and humidity.

The experiments to be conducted in this outdoor chamber are designed to furnish information on what effects a reduction in ambient hydrocarbon levels will have on air quality. In the coming years increased control of both mobile and stationary sources will result in lower atmospheric levels of hydrocarbons. Some evidence concerning the effect of hydrocarbon control on oxidant exists. However, what effect reduced hydrocarbon levels will have on the rate of formation of NO_2 is entirely unknown. There is some evidence to suggest that, within certain ranges of HC and NO_x levels, a decrease in hydrocarbon level can lead to an increase in NO_2 formation.

To determine the effect of varying hydrocarbon levels on NO_2 formation, experiments will be carried out by filling the

chamber with the rural air and then injecting equal concentrations of NO_x into both sides of the chamber. Different concentrations of a synthetic atmospheric hydrocarbon mixture will then be added to each side. Since all conditions in both halves of the chamber will be identical except for the hydrocarbon concentration, the effect of the hydrocarbon level on the conversion of NO to NO_2, the NO_2 maximum and the NO_2 dosage can be observed directly.

C. The Role of Aerosols in Photochemical Smog - Arthur Levy

A. Levy discussed the research planned for the Battelle smog chamber to furnish information on the role of aerosols in photochemical smog formation. Battelle has just initiated a program under EPA sponsorship to follow the number, size, and volume distribution of aerosol particles produced in the smog process. Previous smog chamber studies have been limited to defining aerosols strictly in terms of light scattering. In the present program, besides developing the standard smog parameters and light scattering profiles, the growth and development of particles from about .01 microns to possibly 10 microns in diameter will be followed. Particle size distribution curves will be developed for aerosols produced from specific hydrocarbon nitric oxide systems as well as auto exhaust systems.

Previous work at Battelle showed that mechanical stirring in the chamber significantly reduced the concentration of light scattering aerosols. To study this effect in greater detail, individual hydrocarbons (toluene and hexene) will be irradiated in the chamber with and without SO_2 and with and without stirring.

Also among the studies planned for the smog chamber is an investigation of the inhibition of aerosol formation with hydrocarbon mixtures. Prior work has indicated that the formation of light-scattering aerosol may be markedly lower in systems composed of certain mixtures of hydrocarbons. This was particularly apparent

in a mixture containing several aromatics where considerably less aerosol was produced than in a system containing a single aromatic. Studies are planned to elucidate the chemistry responsible for this effort.

Another anomaly that is under investigation is the fact that considerably less light scattering is produced in smog chambers than in the atmosphere. Likewise, eye irritation measurements are generally lower in chamber studies than in the polluted atmosphere. This latter effect may imply that photochemically-produced aerosol is an eye irritant. Chamber studies on auto exhaust samples are also planned to elucidate the effect of primary aerosol on the formation of secondary aerosol. The auto exhaust studies will be conducted with exhausts from leaded as well as nonleaded fuels generated from cars that have been driven only with the leaded or nonleaded fuels. Previous studies indicated that the concentration of particulates present in auto exhaust is an important variable affecting the formation of photochemical aerosols. Studies will be carried out with varying particulate loading of the auto exhaust samples to elucidate this effect.

IV. THE ROLE OF ATMOSPHERIC MEASUREMENTS IN MODELING

A. Recommendations for Future Field Studies - Alan Eschenroeder

A. Eschenroeder commented on the type of field measurements he feels are needed to aid in the validation of photochemical simulation models. Some of the suggestions he offered were:

1. Vertical profiles of temperature and concentration should be obtained. All of the advanced air pollution simulation models consider the effects of dispersion, horizontal advection and vertical spread of pollutants. Ground-based monitoring stations provide only a small part of the needed information. The gathering of data in three dimensions is essential to the validation of the models.

2. Current validation efforts are hindered by the sparcity of hydrocarbon measurements, both in the number of monitoring stations taking the measurements and in the frequency of the readings. In future studies more measurements should be taken even if it means trading off a few detailed analyses for more frequent readings of only total and non-methane hydrocarbons

3. Results of the current GRC validation effort showed that, while the observed build-up of CO and hydrocarbon during morning peak traffic correlated well with literature values of emission fluxes and atmospheric diffusion coefficients, the build-up of NO_x did not. Using the tabulated emission rates in the model grossly overpredicted the early morning build-up of NO_x.

Due to an apparent heterogeneous uptake of nitrogen oxides, the published values of emission rates had to be reduced by a factor of four to offset the loss. This was consistent with the findings of one other modeling group; however, the remaining two groups did not find it necessary to adjust the tabulated NO_x emission rates. An effort should be made to identify the atmospheric removal processes for the oxides of nitrogen so that appropriate sink mechanisms can be incorporated into the models.

4. Another area of needed research is to ascertain the influence of concentration inhomogenieties upon atmospheric rates of reaction. Due to atmospheric turbulence and the incomplete mixing of pollutants that results, nonuniformities in concentrations arise. The most obvious effect of this turbulence is that the equilibrium balance between NO and O_3 can be upset. Simultaneous chemiluminescence measurements of NO and O_3 taken at 4 a.m. in New York showed that far higher readings of O_3 were obtained than can be calculated on the basis of the $NO/O_3/NO_2$ equilibrium. If this effect is real, using literature values of the rate constant for the reaction of NO and O_3 in simulation models may result in an overestimation of the levels of NO_2 and an underestimation of NO and O_3 concentrations. The magnitude of this phenomenon should be determined before carrying out extensive validation efforts on time-averaged air quality data that may be invalid. As a provisional measure, atmospheric samples could be drawn through a multiple-inlet sampler equipped with a mixing chamber in order to eliminate the effects of inhomogenieties.

Discussion

Chemists and modelers took opposing views in regard to the importance of turbulence effects. Most of the chemists felt that Eschenroeder was magnifying the degree of non-mixedness in the atmosphere and hence, the importance of its effect on the chemistry. Many felt that this effect might be important at ground level due to local sources, but that inhomogenieties should not be as critical at higher altitudes. Eschenroeder made a plea for strip charts of simultaneous O_3 and NO readings so that he could determine whether or not the turbulence effect was serious. At the moment, he did not feel that enough evidence was available to determine just how important this effect might be.

P. Roth made the statement that, in his modeling of the Los Angeles data, he did not find it necessary to reduce the emission rates of NO_x in order to describe the early morning build-up of oxides of nitrogen. He claimed that he obtained a reasonable fit using the literature values of emission fluxes. It was brought out that PES also could fit the observed build-up of NO_x without reducing the emissions, but that Systems, Science and Software, another concern engaged in model validation, could not achieve a fit using tabulated emission fluxes. Eschenroeder re-emphasized the need to carry out NO_x loss studies to determine if such an uptake of NO_x is occurring on the atmosphere.

P. Roth added three more areas of inquiry to the list

of topies for future investigations: 1) Aerosol characterization studies followed by smog chamber studies of systems charged with synthetically generated aerosols having the general characteristics of atmospheric aerosols, 2) Identification and measurement of such species as HNO_3, HNO_2, H_2O_2, aldehydes and PAN, and 3) Studies to ascertain the range of conditions under which the assumption of the integrity of an air parcel is valid.

R. Martinez closed the discussion by re-emphasizing the need for more measurements in order that further refinements in the model may be made and that many of the points in debate at this meeting could be solved. He re-emphasized the urgency to obtain vertical concentration gradients, mixing depths and adequate hydrocarbon measurements. He also emphasized the need to acquire better rate constant data in order to reduce the degrees of freedom in the chemical models and minimize the tendency to curve fit

B. Los Angeles Reactive Pollutant Study - William A. Perkins

W. Perkins commented on the atmospheric measurement program planned for the Los Angeles Basin during the 1973 smog season. This study is designed to furnish information on the fate of reactive pollutants in the atmosphere. The undertaking is a joint effort by the Coordinating Research Council and by the Chemistry and Physics Laboratory and the Division of Meteorology.

The objective of this program is to provide a data base suitable for developing and testing photochemical models. The primary emphasis of this study will be on the gaseous reactive pollutants. The basic concept of this program involves the premise that a moving block of air can be identified and followed as it moves downwind. Three tetroons will be launched simultaneously to identify the air parcel. An atmospheric tracer, released from an aircraft, will be used to indicate diffusion and vertical movements. The air parcel will be tracked by two helicopters at different altitudes and by a ground mobile unit. Aerometic measurements will be made of O_3, NO, NO_2, CO, non-methane HC, and UV intensity. Bag samples will be collected for subsequent GC analysis of the individual hydrocarbons. By following an air parcel, rather than sampling from ground stations that see a succession of air parcels with various ages of reactants, it is anticipated that changes in the nature of the pollutants as they undergo reactions can be observed directly.

C. Coupling of the Photochemistry to an Airshed Model - Ralph C. Sklarew

R. Sklarew of the Models Development Branch in the Division of Meteorology is project officer for the three contracts in photochemical modeling.

R. Sklarew commented on some of the difficulties that must be solved before the full potential of photochemical models as predictive tools for the assessment of air quality can be realized.

One of the problems of current concern is how to incorporate the chemistry into the airshed models. The difficulties in coupling photochemical mechanisms with the meteorological models stem from the basic formulation of the two types of models under development. These are the trajectory or moving coordinate models and the grid or fixed coordinate models. The trajectory model focuses on a volume of air that moves with local mean wind speed through the airshed. Chemical reactions are simulated within this volume of air. Source emissions are added as the volume flows over the source. In essence, the trajectory can be viewed as a moving chamber into the bottom of which pollutants are continually being injected and inside of which chemical reactions are occurring. In this system, the chemistry can be handled with almost as much ease as in a static smog chamber. On the other hand, the grid type model is formulated by subdividing the airshed into 3-dimensional stationary cells and the polluted air is simulated as it passes from

cell to cell. While the trajectory approach emphasizes the natural reference frame in which chemical reactions are occurring, the grid approach forces the reactions to be simulated in a system that is not moving. Errors in following chemical reactions in this stationary system can result. On the other hand, the fixed reference frame of the grid model is the preferred one for calculating the effects of diffusion and the contributions from point sources. Currently efforts are underway to develop a hybrid type of model using the best features of both the fixed and moving coordinate approach.

Another difficulty that must be resolved is that, at present, the effects of local point sources cannot be included accurately in the models. Point sources are presently handled by smearing the emissions over an entire grid. Because of this smearing of pollutant concentrations over a wide area, the scale of resolution of all of the models is poor. Efforts are currently underway to determine means for handling localized concentrations in order to improve spacial resolution.

Although the present accuracy of the models is limited, the models can be used in their present form to simulate the relative effects of control strategies. For example the models are currently being used to evaluate proposed transportation control strategies. The models are first used to simulate the observed pollutant levels using present emissions. Then, the traffic control strategy is translated into emission reductions and the photochemical model is again used to simulate the pollutant levels after the control.

Discussion

During the meeting several individuals indicated that they did not have a clear idea of the objectives of the modeling program. W. Perkins, in particular, asked what purpose EPA expects models to serve. R. Papetti responded by stating that one of the main uses EPA expects to make of its models is to assess the effects of alternative control strategies. Given a choice among several control measures, models will be used to determine which one of the measures should be adopted in order to achieve the greatest reduction in pollutant levels. A major use of models will be to determine long-term air pollution control strategies in terms of their economic impact. Along these lines, models will be used by the states to aid them in formulating their implementation plans. Another use of models will be for land planning so that projected power plants and freeways may be located where their air pollution is minimized. Another important use of models will be to establish short-term strategies so that impending air pollution episodes may be anticipated and consequently prevented. Papetti also spoke of the possibility of using models as a tool for predicting source signatures. Given a map of the distribution of pollutants, it may be possible to use models to identify the sources of these pollutants. It may also be possible to use models to interpolate air quality between monitoring stations. This interpolation could be both spatial and temporal. In essence, modeling of this nature would fill out the picture, giving a far more detailed description of a region's air quality than can be

gotten from scattered monitoring stations. The last potential use of models that Papetti mentioned would be to identify the impact of major changes on air quality. An example of this use of models would be to assess the result of new energy demands brought about by large population growths or through changes in life styles.

D. Summary

The proceedings of this modeling workshop illustrated the fact that considerable resources are being expended by EPA to develop photochemical models to assess air quality. The scale of the efforts of both the Chemistry and Physics Laboratory and the Division of Meteorology was apparent from the presentations and discussions that took place in the two days. Many of the activities that the Chemistry and Physics Laboratory is engaged in to elucidate the chemistry of atmospheric transformation processes were discussed. Descriptions were given of smog chamber studies at the University of North Carolina and Battelle Memorial Institute, the Los Angeles atmospheric measurement program, the St. Louis RAPS undertaking, studies to define the role of aerosols, new instrumental techniques to aid in the identification of trace contaminants, and the efforts underway to employ these data to develop a photochemical mechanism. The Division of Meteorology commented on their efforts to compile emission inventories, air quality and meteorological data and to develop numerical techniques to carry out computer simulations. Many of the discussions were based on the efforts of their contractors to model photochemical smog formation in the Los Angeles Basin.

The problems confronting the development of photochemical models were explored during the two days. A set of chemical reactions were reviewed and an assessment was made of the suspected relevancy of each reaction in describing atmospheric transformation

processes. In addition, those reactions for which the rates of reaction are unknown or imprecisely determined and those reactions for which the intermediates and products are unknown were determined. Suggestions were offered on the type of smog chamber systems to be studied, the measurements that should be made, the desired accuracy of these measurements, the various chamber effects that ought to be elucidated, and the reaction product species that ought to be monitored. The paucity of atmospheric data available for model validation were discussed and recommendations concerning the types of measurements that should be made in future studies were put forth. The many complex problems associated with the non-chemical aspects of modeling were discussed. The many uncertainties in emission inventories, meteorological variables and air quality data were also explored.

It is hoped that these lengthy discussions were beneficial to both the modeler and the chemist. Few problems were solved. But problem solving was not the intent of this workshop. The intent was to define the problems and to make recommendations for areas where further research is needed. The recommendations that were made during this workshop can be separated into these general areas:

1. Basic Chemistry

    a. Obtain better means for determining $k_a\emptyset$.

    b. Determine the effects of surface-to-volume ratio on the rates of formation of HNO_3 and HONO.

    c. Determine rate constants for the reactions of alkoxy radicals.

d. Better determine the quantum yields of aldehyde photolysis as a function of wavelength.

e. Determine the products of the reactions of olefins with OH, O, and O_3 under atmospheric conditions.

2. Smog Chamber Experiments

a. Measurements of species should be made in situ whenever possible.

b. Nitrogen balances should be obtained, if possible.

c. Experiments should be carried out at concentrations approximating projected air quality levels.

d. Effects of aerosols should be studied by carrying out chamber runs with varying particulate loading.

e. Careful control of light intersity, relative humidity, temperature, and initial NO_2 concentration should be made.

f. The precision and accuracy of all measurements should be reported.

g. More complete product identification and analysis, especially for HNO_3, HONO, H_2O_2, and PAN, should be made.

3. Atmospheric Measurements

a. Vertical concentrations and temperature profiles should be obtained.

b. Mixing depths and wind speeds aloft should be determined.

c. Atmospheric removal processes for NO_x should be identified.

d. The influence of concentration inhomogenieties upon atmospheric rates of reaction should be determined.

e. Aerosol characterization studies should be made.

f. Detection in the atmosphere of such species as HNO_3, HNO_2, and H_2O_2 should be made, if possible.

To achieve success in this modeling venture, it is imperative that chemists and modelers work together. To ignore each others expertise in his particular field of endeavor, to insist on a duplication of efforts, or to stress one's own interests at the exclusion of the other can only impede progress in this endeavor. Better lines of communication between experimentalist and modelers were established during this workshop and hopefully new impetus to the modeling program will come about as a consequence of this meeting.

APPENDIX A

The Chemistry of Photochemical Smog Formation

	Reaction	Comments
1	$NO_2 + h\nu \rightarrow NO + O$	$k_a\emptyset$ uncertain by ∿20%; difficulties encountered in trying to relate measured k_d to $k_a\emptyset$.
2	$O + O_2 + M \rightarrow O_3 + M$	Well known; $k = 2.0 \times 10^{-5}$ ppm^{-2} min^{-1}
3.	$O_3 + NO \rightarrow O_2 + NO_2$	$20 \leq k \leq 40$ ppm^{-1} min^{-1}.
4.	$O_3 + NO_2 \rightarrow NO_3 + O_2$	Two measured values, 0.11 and 0.048 ppm^{-1} min^{-1}, both of which may be too high.
5.	$NO_3 + NO_2 \rightarrow N_2O_5$	k_5 and k_6 uncertain by ∿20%; equilibrium constant is very temperature dependent.
6.	$N_2O_5 \rightarrow NO_3 + NO_2$	
7.	$N_2O_5 + H_2O \rightarrow 2HNO_3$	Reaction in gas phase is negligible; reaction occurs only on surfaces.
8.	$NO_3 + NO \rightarrow 2NO_2$	k factor of 10^2 uncertainty; most important NO_3 removal process.
9.	$NO_3 + h\nu \rightarrow NO_2 + O$	Importance not determined.
10.	$NO + NO_2 + H_2O \rightarrow 2HONO$	Rate may be higher than first order with respect to H_2O; heterogeneous contributions to this rate not determined.
11.	$2HONO \rightarrow NO + NO_2 + H_2O$	
12.	$HONO + h\nu \rightarrow OH + NO$	$k_{12} \sim 0.1\ k_a\emptyset$; photolysis of HONO in early morning may initiate smog formation.
13.	$OH + NO_2 + [M] \rightarrow HNO_3 + [M]$	k uncertain; order of reaction depends on pressure of M; probably second order in atmosphere.
14.	$OH + NO + [M] \rightarrow HONO + [M]$	k uncertain; pressure dependence not determined.

	Reaction	Comments
15.	$OH + CO \rightarrow CO_2 + H$	$230 \leq k \leq 280$ ppm^{-1} min^{-1}; reaction is too slow to compete with olefin - OH reactions.
16.	$H + O_2 + M \rightarrow HO_2 + M$	Only atmospheric reaction of importance for H atoms.
17.	$HO_2 + NO \rightarrow HO + NO_2$	$10^2 \leq k \leq 10^3$ ppm^{-1} min^{-1}; most important HO_2 removal process.
18.	$2HO_2 \rightarrow H_2O_2 + O_2$	k uncertain by $\sim$50%.
19.	$H_2O_2 + h\nu \rightarrow 2OH$	Photolysis rate in sunlight not well known.
20.	Paraffins + $O \rightarrow R + OH$	k uncertain by $\sim$ factor of ten.
21.	Paraffins + $OH \rightarrow R + H_2O$	k uncertain by $\sim$ factor of ten.
22.	Olefins + $O \rightarrow$?	k factor of 2 uncertainty; products of reaction under atmospheric conditions unknown.
23.	Olefins + $OH \rightarrow$?	Most important olefin reaction; products of reaction unknown.
24.	Olefins + $O_3 \rightarrow$ Aldehyde + Zwitterion	k factor of 2 uncertainty; reactions of Zwitterion unknown.
25.	Olefins + $H_2O \rightarrow$?	Probably unimportant.
26.	Aromatics + $O \rightarrow R + OH$	k's for most reactions unknown; $k_{26} \sim k_{20}$.
27.	Aromatics + $OH \rightarrow R + H_2O$	k's for most reactions unknown.
28.	$RCHO + h\nu \rightarrow R + HCO$	Quantum yields as function of $h\nu$ not well known; k_{28} may be an important chain initiation step in atmosphere.
29.	$RCHO + h\nu \rightarrow RH + CO$	
30.	$RCHO + OH \rightarrow RCO + H_2O$	$k \sim 10^4$ ppm^{-1}min^{-1}.
31.	$RCHO + O \rightarrow RCO + OH$	Slow compared to R_x 30.
32.	$HCO + O_2 \rightarrow HO_2 + CO$	k high; only important HCO reaction.

	Reaction	Comments
33.	$RCO + O_2 \rightarrow RC(O)OO$	Only RCO reaction of importance.
34.	$RC(O)OO + NO \rightarrow R + CO_2 + NO_2$	k unknown.
35.	$RC(O)OO + NO_2 \rightarrow RC(O)OONO_2$	k unknown.
36.	$R + O_2 \rightarrow RO_2$	Very fast.
37.	$RO_2 + NO \rightarrow RO + NO_2$	k unknown.
38.	$RO_2 + NO_2 \rightarrow RO_2NO_2$	k unknown.
39.	$RO_2 + HO_2 \rightarrow ROOH + O_2$	k unknown.
40.	$RO + O_2 \rightarrow RCHO + HO_2$	k unknown.
41.	$RO + NO \rightarrow RONO$	k unknown.
42.	$RO + NO_2 \rightarrow RONO_2$	k unknown.

APPENDIX B -/

Workshop Participants

Fred N. Alyea
General Electric Company
P.O. Box 8555
Philadelphia, Pennsylvania 19101

Theodore Baurer
General Electric Company
P.O. Box 8555
Philadelphia, Pennsylvania 19101

Joseph V. Behar
University of California
Statewide Air Pollution Research Center
Riverside, California 92505

James F. Black
Esso Research and Engineering Company
P.O. Box 51
Linden, New Jersey 07036

M. H. Bortner
General Electric Company
P.O. Box 8555
Philadelphia, Pennsylvania 19101

Raymond J. Campion
Esso Research and Engineering Company
P.O. Box 51
Linden, New Jersey 07036

David P. Chock
General Motors Research Laboratories
Fuel and Lubricants Department
Warren, Michigan 48090

Kenneth L. Demerjian
Ohio State University
Department of Chemistry
Columbus, Ohio 43210

Alan Eschenroeder
General Research Corporation
P.O. Box 3587
Santa Barbara, California 93105

Donald L. Fox
University of North Carolina
School of Public Health
Chapel Hill, North Carolina 27514

William A. Glasson
General Motors Research Laboratories
Fuel and Lubricants Department
Warren, Michigan 48090

David M. Golden
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, California 94025

Thomas A. Hecht
California Institute of Technology
Spalding Laboratory 208-41
Pasadena, California 91109

Dale G. Hendry
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, California 94025

Harvey Jeffries
University of North Carolina
School of Public Health
Chapel Hill, North Carolina 27514

Harold S. Johnston
University of California
Department of Chemistry
Berkeley, California 94720

Richard Kamens
University of North Carolina
School of Public Health
Chapel Hill, North Carolina 27514

Arthur Levy
Battelle Memorial Institute
Atmospheric Chemistry and Combustion Systems Division
505 King Avenue
Columbus, Ohio 43201

Hiram Levy III
Astrophysical Observatory
60 Garden Street
Cambridge, Massachusetts 02138

Alan C. Lloyd
University of California
Statewide Air Pollution Research Center
Riverside, California 92502

Jose R. Martinez
General Research Corporation
P.O. Box 3587
Santa Barbara, California 93105

Hiromi Niki
Ford Motor Company
Scientific Research Staff
Dearborn, Michigan 48121

William A. Perkins, Jr.
Metronics Associates, Inc.
3201 Porter Drive
Palo Alto, California 94304

James N. Pitts, Jr.
University of California
Statewide Air Pollution Research Center
Riverside, California 92502

Lyman A. Ripperton
University of North Carolina
School of Public Health
Chapel Hill, North Carolina 27514

Philip M. Roth
Systems Applications, Inc.
9418 Wilshire Blvd.
Beverly Hills, California 90212

Lowell G. Wayne
Pacific Environmental Services, Inc.
2932 Wilshire Blvd.
Santa Monica, California 90403

Karl Westberg
Aerospace Corporation
P.O. Box 95085
Los Angeles, California 90045

Environmental Protection Agency
Chemistry and Physics Laboratory
Research Triangle Park, North Carolina 27711

A.P. Altshuller
Joseph J. Bufalini

EPA (continued)

Marijon M. Bufalini
Basil Dimitriades
Marcia Dodge
Alfred H. Ellison
Philip L. Hanst
Stanley L. Kopczynski
Charles F. Walters
William E. Wilson

Division of Meteorology
Research Triangle Park, North Carolina 27711

Warren B. Johnson
Francis Pooler, Jr.
Ralph C. Sklarew

EPA, Washington, D.C.

Robert Papetti
Processes and Effects Division
4th and M Streets
Washington, D.C. 20460